

COMPOSITE MOLDED PARTS COMPRISING A FILM COATING AND METHOD FOR PRODUCING THE SAME

Specification

The present invention relates to methods for producing composite molded parts with a film coating, the composite molded parts thus obtained, and their use as interior or exterior vehicle body parts, as components for shipbuilding and aircraft construction, or as components for household or electrical appliances.

Composite molded parts from a plastic molding composition provided with a film are known to one skilled in the art. Instead of lining plastic components with a film or adhesively bonding such a film, today in industrial applications increasingly what is done is for the films to be rear-injected, rear-pressed or foam-backed directly in the shaping tool along with the plastic molding composition (A. Grefenstein, "Folienhinterspritzen statt Lackieren, Neue Technik für Karosseriebauteile aus Kunststoff" [Film Rear- Injection Instead of Painting: Novel Technique for Plastic Vehicle Components], in Metalloberfläche [Metal Surface] 10/99, Vol. 53, Carl Hanser Verlag, München, 1999). In this way, in a single operation, the desired composite molded part is achieved without requiring further process steps.

In German Patent Disclosure DE-A 19928774, a method is described in which multi-layer films are rear-injected by injection molding using thermoplastic materials. By using multi-layer films, it is possible to provide the components with decoration and optionally with a protective layer, so that later painting can be dispensed with. What is obtained is composite molded parts that are distinguished by good rigidity and high fracture strength and that can be considered for instance as components for vehicle body construction. These usually large-area components, however, have a relatively high intrinsic weight, which makes them appear disadvantageous in some cases for components on the roof of vehicles. Moreover, such components can have a variable mechanical load-bearing performance, depending on the direction. The same is true for the thermal elongation - which particularly in automobile construction is a critical variable - typically called the CTE value (for coefficient of thermal elongation, in accordance with DIN 53752).

Particularly with fiber-reinforced injection-molded components as well as fiber-reinforced film rear-injected or film-rear-pressed composite molded parts, warping of the entire component can sometimes be found, which makes the component completely useless (see among other sources Technische Information [Technical Information] 05/99, BASF AG), for instance if high fitting accuracies are required, as in the case of construction of vehicle body or housing components.

European Patent Disclosure EP-A 995 667 discloses composite molded parts foam-backed with polyurethane and a method for producing them. Foam-backed composite molded parts, however, have a profile of properties that is not suitable for all component applications. In particular, it would be desirable to achieve better film adhesion and thus a higher heat distortion point of the component as well as recycling of the material of the entire composite. Unlike the rear injection method, lower pressures occur in the foaming tool, generally in the range from 3 to 10 bar. As a rule, however, these are not sufficient to iron out surface flaws after the thermoforming of the film. Moreover, unless special additional provisions are made, such as flame-treating the film or using adhesive agents, adhesion problems between the film and the foam-backing composition are often unavoidable (see also EP-A 995 667).

In the method for producing composite molded parts in German Patent Disclosure DE-A 1 942 494 as well, in which a PVC film is for instance deep-drawn in the injection molding tool and then a foaming agent containing a plastic molding composition is rear-injected, an adhesion promoter or welding aid promoter is mentioned, for obtaining adequate adhesion between the film and the rear injection material.

From International Patent Disclosure WO 99/63019, it is known that components of thermoplastic elastomers can be created with an especially fine-pored structure by using carbon dioxide or nitrogen, for instance, in supercritical form as the foaming agent. However, this reference does not mention composite molded parts or their production.

It was therefore the object of the present invention to make composite molded parts available that are distinguished by a uniform/isotropic profile of thermal and mechanical properties, that can be produced in a simple way and particularly in mass production, and that are superior in terms of rigidity and breakage behavior to conventional components. Moreover, composite molded parts are to be obtained that in terms of their appearance on the film side meet all the requirements made of a so-called Class-A surface.

Accordingly, composite molded parts have been discovered that are obtained in that a single- or multi-layered film is inserted into a tool.

As the films, both single-layer films and films with two or more layers can be considered. Preferably, films with two or more layers, that is, composite laminated films, will be used.

Suitable single-layer films are formed for instance from mixtures of polyamides and polyethylene ionomers, such as ethene/methacrylic-acid copolymers, for instance containing counterions of sodium, zinc and/or lithium (obtainable on the market, among

other sources under the trade name Surlyn®, made by DuPont), or from copolymers. However, all the other currently used single-layer films can also be employed, such as PVC, ABS, ASA, polyester, or polycarbonate films.

Composite laminated films composed of at least one substrate layer (1), optionally at least one intermediate layer or decorative layer (2), and at least one transparent cover layer (3), in that order, are especially suitable.

The substrate layer (1) generally includes thermoplastic polymers, such as ASA polymers, ABS polymers, polycarbonates, polyesters such as polyethylene terephthalate or polybutylene terephthalate, polyamides, polyether imides, polyether ketones, polyphenyl sulfides, polyphenylene ethers, or mixtures of these polymers. For the substrate layer, ASA polymers are preferably used. Preferably, blends of ASA polymers and/or ABS polymers with polycarbonates or polybutylene terephthalate are used.

The term ASA polymers is understood in general to mean styrene-acrylonitrile polymers with modified impact strength, in which graft copolymers of vinyl aromatic compounds, in particular styrene, and vinyl cyanides, in particular acrylonitrile, on polyalkyl acrylate rubbers in a copolymer matrix, in particular of styrene and acrylonitrile are present. ASA polymers can be obtained on the market, for instance under the name Luran® S (BASF AG).

Suitable polycarbonates are known per se. Especially preferred polycarbonates are those based on bisphenol A, or bisphenol A together with up to 80 mol-% of further aromatic dihydroxy compounds. Examples of commercially available polycarbonates are Makrolon® (Bayer) and Lexan® (GE Plastics B.V.). Copolycarbonates based on bisphenol A and for instance bis-(3,5-dimethyl-4-hydroxyphenyl)sulfone and 1,1-di-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexyl, which are distinguished by a high heat distortion point can also be considered. This last copolycarbonate is also commercially available under the trade name Apec®HT (Bayer AG). The polycarbonates can be used both as a ground product or in granulated form. As a mixture ingredient, especially in an ASA substrate layer, they are typically present in quantities of from 0 to 60 weight-%, preferably from 20 to 50 weight-%, in each case referred to the entire molding composition.

Instead of ASA polymers or blends of them with polycarbonates, or in addition to the latter, the substrate layer (1) can also be constructed of ABS polymers (which means among others modified high-impact styrene-acrylonitrile polymers, in which graft copolymers of styrene and acrylonitrile are present on polybutadiene rubbers in a copolymer matrix of styrene and acrylonitrile), mixtures of poly(meth)acrylates and SAN polymers, which can be high- impact-modified with polyacrylate rubbers, such as Terlux®

(BASF AG), polycarbonates, polyesters, such as polybutylene terephthalate (PBT) (such as Ultradur®, BASF AG) or polyethylene terephthalate (PET), polyamides (Ultramid®, BASF AG), polyether imides (PEI), polyether ketones (PEK), polyphenylene sulfides (PPS), polyphenylene ethers, or blends of these polymers. The aforementioned polymer materials are widely known, for instance from H. Dominginghaus, Die Kunststoffe und ihre Eigenschaften [Plastics and their Properties], VDI-Verlag, Düsseldorf (1992).

In a preferred embodiment, the substrate layer (1) is formed from ASA polymers, mixtures of ASA polymers and polycarbonates, ABS polymers, polycarbonates, polybutylene terephthalate, polyethylene terephthalate, polyamides, or blends of ASA polymers and polybutylene terephthalate. Especially preferably, the substrate layer (1) includes a molding composition of ASA polymers or mixtures of ASA polymers and polycarbonates. It can also substantially or entirely comprise these polymers.

The layer thickness of the substrate layer (1) is preferably 100 to 2000 µm, in particular 150 to 1500 µm, and especially preferably 200 to 1000 µm.

The substrate layer (1) of can further contain, as additives, such compounds as are typical and usual for the (co)polymers described, such as polycarbonates, SAN polymers, or graft copolymers, and mixtures thereof. Examples of additives that can be named are: dyes, pigments, effect colorants, antistatic agents, antioxidants, stabilizers for improving thermal stability or for increasing lightfastness, and raising the resistance to hydrolysis or chemical resistance, and in particular lubricants, which are expedient for producing molded bodies or molded parts.

The composite laminated films can furthermore have an intermediate layer (2) of thermosetting and/or pressure- setting plastics, optionally with further additives. The intermediate layer (2) is also used as a color-carrying or cover layer. Suitable thermosetting plastics are for instance the polyalkyl and/or aryl esters of (meth)acrylic acid, including in modified high-impact form, poly(meth)acrylamides, or poly(meth)acrylonitrile, also known as acrylic resins, as well as ABS polymers, styrene-acrylonitrile polymers (SAN), polycarbonates, polyesters such as polyethylene terephthalate or polybutylene terephthalate, polyamides, in particular amorphous polyamide, such as polyamide 12, polyether sulfones, thermoplastic polyurethanes, polysulfones, polyvinyl chloride, or ASA polymers. Blends of the above (co)polymers are also fundamentally suitable, such as mixtures of ASA polymers and polycarbonates, as described above for the substrate layer (1). Thermoplastic polyurethanes, in particular weather- resistant aliphatic polyurethanes, such as the commercial product Elastollan® (Elastogran, Lemförde) (see also Kunststoff-Handbuch, Polyurethane [Plastics Handbook, Polyurethanes], Vol. 7, 2nd Ed., Carl Hanser Verlag, München, 1983, pp. 31-39) can be considered as film materials. Acrylic resins, polycarbonates, and/or styrene (co)polymers

are preferably used.

The intermediate layer (2) is preferably constructed of high-impact polymethyl methacrylates (PMMA), polycarbonates, or the ASA polymers described above for the substrate layer (1), or blends of them with polycarbonates.

Suitable modified high-impact poly(meth)acrylates are described for instance in M. Stickler and T. Rhein in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A21, pp. 473-486, VCH publishers, Weinheim, 1992 and H. Domininghaus, Die Kunststoffe und ihre Eigenschaften [Plastics and their Properties], VDI-Verlag, Düsseldorf (1992). Suitable polymethyl methacrylates are furthermore known to one skilled in the art and can be obtained for instance by the trademarks Lucryl® (BASF AG) and Plexiglas® (Röhm GmbH).

As a decorative layer, the intermediate layer (2) can have effect colorants. These are for instance dyes, effect colorants, metal flecks, or pigments. Organic or inorganic compounds can be considered as dyes or pigments. Multicolored, white and black pigments (colored pigments) and liquid crystal pigments can be named as organic pigments. Once again both colored pigments and gloss pigments and the usual inorganic pigments used as fillers are suitable as inorganic pigments.

In a further embodiment, the substrate layer (1) - alone or together with an optionally present intermediate layer (2) - has the aforementioned effect colorants.

The layer thickness of the decorative layer (2) is generally in the range from 10 to 1000, preferably 50 to 500, and especially preferably 100 to 400 μm .

As a rule, the cover layer (3) is translucent, and preferably transparent. It is composed of poly(meth)acrylate polymers, high-impact poly(meth)acrylate, especially high- impact polymethyl methacrylate, fluoro(co)polymers such as polyvinylidene fluoride (PVDF), ABS polymers, polycarbonates, polyethylene terephthalate, amorphous polyamide, polyether sulfones, polysulfones, or SAN copolymers. In particular, the cover layer contains polymethyl methacrylate, high-impact polymethyl methacrylate, or polycarbonates, preferably polymethyl methacrylate, high-impact polymethyl methacrylate, PVDF, or mixtures thereof. The polymers and their mixtures are as a rule selected such that they lead to a transparent cover layer.

In a further embodiment, the cover layer originates in a radiation-curable composition, which contains functional groups that can be cured both ionically and in particular radically. The radically radiation-curable cover layer includes preferably i) polymers with ethylenically unsaturated groups or ii) mixtures of these polymers with ethylenically

unsaturated low-molecular compounds or iii) mixtures of thermosetting plastics without ethylenically unsaturated groups with ethylenically unsaturated compounds.

In polymer i), for ethylenically unsaturated groups, it is possible for instance to use maleic acid, fumaric acid, maleic acid anhydride, or (meth)acrylic acid radicals. Suitable polymers i) can be based on polyesters, polyethers, polycarbonates, polyepoxides, or polyurethanes.

As ethylenically unsaturated low-molecular compounds, the following can for instance be considered: alkyl (meth)acrylates, such as methyl methacrylate, methyl acrylate, n-butyl acrylate, ethyl acrylate, or 2-ethylhexyl acrylate; vinyl aromatic compounds, such as vinyl toluene or styrene; vinyl esters, such as vinyl stearate or vinyl acetate; vinyl ethers, such as vinyl methyl ether, acrylonitrile, or methacrylonitrile.

Suitable saturated thermoplastic polymers are for instance polymethyl methacrylate, high-impact polymethyl methacrylate, polystyrene, high-impact polystyrene (HIPS), polycarbonate, or polyurethanes.

The radiation-curable composition can also contain, as further ingredients, photoinitiators, flow-control agents, or stabilizers, such as UV absorbers and radical absorbers.

The radiation curing of the cover layer is done with high-energy radiation, such as UV light or electron radiation, optionally at elevated temperatures.

For further details of the composition of the radiation-curable cover layer and its production, WO 00/63015 is expressly referred to here.

An adhesive layer of an adhesion promoter, with a layer thickness of in general 5 to 400 and in particular 5 to 100 μm can adjoin the outer surface of the substrate layer. The adhesion promoter serves to establish a solid connection with a selected substrate that comes to be located below the substrate layer (for instance as a result of rear injection). The adhesion layer is used whenever the adhesion of this further substrate to the substrate layer is inadequate (for instance in the case of polyolefin substrates). Suitable adhesion promoters are known to one skilled in the art. Examples of suitable adhesion promoters are ethylene vinyl acetate copolymers for coupling to polyethylene, and maleic acid anhydride-grafted polypropylenes for coupling to polypropylene. In both cases, according to current thinking, the adhesion is achieved by incorporating polar groups into the nonpolar polyolefins.

The composite laminated films are produced among other ways by adaptor or nozzle

coextrusion of the components, preferably in a single-stage process. Nozzle coextrusion is explained for instance in EP-A2 0 225 500; the adaptor coextrusion process is described in the proceedings of the **Extrusionstechnik** [Extrusion Technology] Conference entitled "Coextrusion von Folien" [Coextrusion of Films], October 8 and 9, 1996, VDI-Verlag Düsseldorf, particularly in the paper presented by Dr. Netze. The composite laminated films can also be produced by laminating the individual film layers to one another in a heatable gap. However, a three-layer film can for instance be produced beginning with a composite laminated film comprising the two layers (2) and (3), by retroactively providing them with a substrate layer (1).

The film with one, two, three or more layers can be placed as is or in deep-drawn or thermoformed form into the molding tool. It is also possible not to perform the deep- drawing or thermoforming process until inside the rear injection or rear-pressing tool. It is furthermore possible to provide the surface of the film with a decorative structure, such as scarring, in the rear injection or rear- pressing process or in the deep-drawing or thermoforming process, by the choice of a suitable tool surface. It is understood that this surface structuring can also be done in a separate step.

All the known thermoplastic molding compositions are suitable plastic materials.

Preferably as the plastic materials, thermoplastic molding compositions on the basis of ASA polymers, ABS polymers, or SAN polymers, poly(meth)acrylates, polyether sulfones, polybutylene terephthalate, polycarbonates, polypropylene (PP) or polyethylene (PE), or mixtures thereof, are used. Blends of ASA polymers and/or ABS polymers with polycarbonates or polybutylene terephthalate are preferred, especially blends of ASA polymer with polycarbonates or polybutylene terephthalate, as well as mixtures of polycarbonate and polybutylene terephthalate. Fundamentally, amorphous thermosetting plastics are preferred.

The aforementioned plastic materials and mixtures thereof can have further typical adjuvants and fillers. Such adjuvants are for instance lubricants or unmolding agents, waxes, effect colorants, for instance pigments such as titanium dioxide or dyes, flame retardants, antioxidants, stabilizers, for instance to protect against the influence of light, or antistatic agents.

As particulate fillers, it is also possible to use soot, sawdust, amorphous silicic acid, magnesium carbonate, powdered quartz, mica, bentonite, talcum, calcium carbonate, glass beads, feldspar, or in particular such calcium silicates as wollastonite and kaolin.

The plastic material used for the rear injection or rear-pressing contains fibers, which

are also understood to include chiplike products, such as preferably fiber-reinforced ABS polymer or a fiber-reinforced PBT-ASA mixture. The fibers are present in the plastic material in general in a quantity of from 3 to 40 weight-%, preferably from 10 to 30 weight-%, and especially preferably from 15 to 20 weight-%, referred to the total weight of the molding composition.

Examples of fibrous fillers that can be named are carbon, aramide, steel or glass fibers, aluminum flakes, cut glass, or glass silk rovings. Glass fibers are especially preferred. As fibers, such natural fibers as flax, hemp, jute, sisal, ramie, or carnafl can also be used.

The glass fibers used can be of E-, A- or C-glass and are preferably equipped with a coat and/or an adhesion promoter. Their diameter is generally in the range from 6 to 30 μm and preferably in the range from 10 to 17 μm . Both endless fibers (rovings) and cut glass fibers (staple), typically with a length of 1 to 30 mm and preferably 3 to 15 mm, or short glass fibers with a length of 0.2 to 0.4 mm as a rule, can be used. Particularly if the plastic material contains or comprises ABS polymer, long glass fibers are used.

As pore-forming foaming agents, both chemical foaming agents and physical foaming agents can be considered.

Suitable chemical foaming agents are fundamentally compounds of the kind that under the influence of heat or a catalyst or upon irradiation with high-energy radiation split off volatile components. In most cases, the foaming agent decomposition is thermally induced (among other sources, see G. Trausch, "Physikalisch und chemisch getriebene Thermoplastschäume, Grenzen der Verfahren und Anwendungen" [Physically and Chemically Aerated Thermoplastic Foams, Limits of the Methods, and Applications], in "Schäume aus der Thermoplastischen Schmelze" [Making Foams from Thermoplastic Melt], VDI-Verlag, Düsseldorf, 1981, pp. 1 to 16. Typically, the foaming agent should be selected such that decomposition preferably occurs only after or during the introduction of the molten plastic material into the molding tool.

Examples of suitable chemical foaming agents that can be named are organic compounds, such as azo compounds, such as azodicarboxylic acid diamide (under the tradename Luvopor®, BASF AG, available on the market), sulfohydrazides, such as p-toluenesulfonic acid hydrazide, such as the commercial product Porofor® (Bayer AG), or 4,4'-oxybis(benzene sulfohydrazide), such as the commercial product Genitron® (Bayer AG), semicarbazides, such as p-toluenesulfonyl semicarbazide, citric acid, and esters thereof (available on the market under the tradename Hydrocerol® HK, Boehringer Ingelheim), peroxy compounds (such as Luperoxe®, made by Akzo), triazine compounds, such as 2,4,6-trihydrazino-1,3,5-triazine, tetrazol compounds, such as 5-phenyltetrazol, tetramine compounds, such as dinitroseptamethylene tetramine, or mixtures of the above

compounds, as well as inorganic compounds, such as alkali or alkaline earth carbonates or bicarbonates, such as calcium carbonate or sodium carbonate (soda), or mixtures thereof. It is understood that arbitrary mixtures of organic and inorganic foaming agents can also be used. Suitable foaming agents are also described in H. Saechting, Kunststoff-Taschenbuch [Plastics Handbook], Carl Hanser Verlag, München, 27th Ed., 1998, pp. 271, 532, and 767 through 768, which is hereby expressly cited. The chemical foaming agents described, depending on their type, split off nitrogen, oxygen, or carbon dioxide. For these compounds, the temperatures of decomposition are generally in the range from 90 to 285°C.

In the plastic material, before decomposition, the chemical foaming agent is typically present in quantities from 0.1 to 5 weight-%, and preferably in quantities from 0.5 to 2 weight-%, referred to the total weight of the forming composition. The quantity of foaming agent is also determined depending on the type of foaming agent, that is, its capacity for liberating volatile components, and on the degree of foaming desired for the particular application.

In addition, nucleation agents can be added to the foaming agents, if necessary, to improve the homogeneity of the pore formation. Suitable nucleation agents are for instance fine-particle silicates (SiO_2), organic bromine compounds, metal oxides such as zinc oxide or magnesium oxide, metal salts, boron nitride, and especially preferably talcum, which is for instance also used in the production of polystyrene foam (tradename Styrodur® from BASF AG; see also K.-D. Kolossow, "Extrusion von geschäumten Halbzeug mit Einschneckenextrudern" [Extrusion of Foamed Semifinished Products with Single-Worm Extruders], in "Handbuch der Kunststoff-Extrusionstechnik" [Handbook of Plastic Extrusion Technology], Carl Hanser Verlag, München, 1986, pp. 423 to 465, or "Kunststoff-Handbuch, Polystyrol" [Plastics Handbook, Polystyrene], Vol. 4, Becker and Braun, Editors, Carl Hanser Verlag, München, 1996, pp. 588 to 603). It is understood that mixtures of the aforementioned nucleation agents can also be employed.

The higher-molecular products of decomposition of chemical foaming agents can also function as nucleation agents.

Suitable additive quantities of nucleation agents are generally in the range from 0.05 to 10 and preferably in the range from 0.1 to 1 weight-%, referred to the total weight of polymer to be foamed.

The chemical foaming agent can be added, for instance in liquid form or in the form of a powder, granulate or pellets, together with the plastic material into the plasticizer unit. It is also possible to mix the foaming agent with the plastic material as a master batch. The plastic molding composition that is the basis of the master batch is preferably identical with

the plastic material for the composite molded part, but is at least partially or completely compatible; that is, complete phase separation does not occur (see also Kunststoff-Handbuch, Die Kunststoffe [Plastics Handbook, The Plastics], Vol. 1, Becker and Braun, Editors, Carl Hanser Verlag, München, 1990, pp. 134 and 135). The foaming agent can be added continuously or in batches and via separate mixers or metering stations, or in the case of liquid foaming agents, via separate metering pumps.

The processing of the plastic melt containing foaming agent can be done in any commercially available injection molding machines and extruders. Advantageously, shutoff nozzles are used, which prevent the foaming agent from causing the melt to foam up already in the metering zone. To prevent foaming in the introduction region of the plasticizer unit, the temperature in this region is typically selected to be below the temperature of decomposition of the foaming agent, if the decomposition is thermally induced. In the compression zone, conversely, the temperature of the composition can already be selected such that volatile components are liberated. Especially advantageously, however, the decomposition of the foaming agent does not occur until inside the molding tool.

It has proved advantageous in the rear injection method to use the highest possible injection speed. Particularly for the sake of making to components with the lightest possible weight, it is also advantageous to dispense with an afterpressure phase.

For both the rear injection and the rear-pressing process, physical foaming agents can also be employed. Suitable examples are ethanol, dimethyl ether, n-butane, n-pentane, the branch-chained pentane compounds and cyclopentane, and the so-called fluorochlorinated hydrocarbons such as R 11, R 12, R 12 B 1, R 12 B 2, R 13, R 13 B 1, R 14, R 21, R 22, R 23, R 32, R 112, R 133, or R 114 (nomenclature per DIN 8962). In addition, nitrogen and carbon dioxide, including in supercritical form, can be considered. Arbitrary mixtures of physical foaming agents can also be employed. Very good results are obtained with supercritical carbon dioxide.

In the rear injection process, the procedure is preferably such that the chemical foaming agent is either admixed with the rear injection material jointly with the glass fibers in the metering funnel, or is added downstream of the glass fiber additive in a downstream region of the plasticizer unit. If the glass fibers are not admixed until during the processing of the rear injection material, then it is recommended that a double-worm extruder be used in combination with a piston-type injection unit, as described in Wobbe and Zimmet, Plastverarbeiter [Plastics Processor] 2001 (52), pp. 52 through 54.

Typically, physical foaming agents are metered into the melt under pressure, preferably in liquid or supercritical form, for instance via a piston pump into the metering zone of the

plasticizer unit. When the melt is introduced into the molding tool, care must be taken that premature foaming of the melt not occur along the flow channel, for instance because of pressure relief in a divergent flow cross section. As a rule, this is achieved by providing that the entire molding tool along with the gate distributor system be designed in a geometrically suitable way, using typical computer simulation programs (for instance from Moldflow Corp., Wayland, Massachusetts).

For the rear injection process, chemical foaming agents that for the most part do not decompose until after introduction into the pressing tool are preferably used. If chemical foaming agents that decompose upon thermal induction are used, this typically requires exact temperature guidance in the plasticizer unit. This is successfully achieved preferably whenever, along with the use of high-precision tempering systems (the cylinder temperature advantageously fluctuates only within the range of at most $\pm 3^{\circ}\text{C}$) the dwell times of the polymer melt in the plasticizer unit are kept constant. Down times should accordingly be strictly avoided.

Another variant method is to use chemical foaming agents that do not decompose thermally but instead decompose only under the influence of high-energy radiation, such as UV radiation, and split off nitrogen in the process. Suitable compounds that can be considered are for instance hydrazides and tetrazones ($(\text{N}(\text{R}_2)\text{N}=\text{NN}(\text{R}_2)$, where $\text{R} = \text{C}_1$ to C_{10} alkyl, C_6 to C_{14} aryl, or benzyl; in a tetrazone compound, R can have various meanings). Such foaming agents are used according to the invention in concentrations of 0.05 to 5%, referred to the polymer weight. This embodiment is especially attractive in the rear-pressing process. The application of the UV radiation is favorably done after the molten strand has been placed in the pressing tool, for instance immediately before the press is closed.

In one embodiment of the method of the invention for the rear injection of films with fiber-reinforced plastic material, both the plastic material and fiber material as well as further additives are placed, before the rear injection operation, in an extruder or an injection molding machine and melted and mixed. In an especially suitable embodiment, the extruder or the injection molding machine, in the zone following the compression zone, has at least one dispersive and preferably a distributive mixing element. Preferably, all the plastic material downstream of the compression zone is in molten form. In extruders, the compression zone is also known as a transition zone (see among others Saechting, *Kunststoff-Taschenbuch* [Plastics Handbook], 27th Ed., Carl Hanser Verlag, München, 1998, pp. 244-247).

As the distributive mixing elements, rhomboid or pinlike or camlike mixing parts or those with openings in the thread course can for instance be considered. Suitable mixing parts are also described in "*Einfärben mit Kunststoffen*" [Dyeing with Plastics], issued by

VDI- Gesellschaft Kunststofftechnik, VDI-Verlag, Düsseldorf, 1975, pp. 261-265. As the mixing element, a separate mixing ring, which is disposed between the housing of the extruder or the injection molding machine (also called the stator) and the worm (also called the rotor), running freely around the worm, and is provided with circumferentially extending rows of openings, is preferably used, known for short as a Twente mixing ring. The openings can have regular or irregular geometric shapes but in general are circular or oval. They can moreover be disposed in random order or in encompassing circular paths on the mixing ring. The worm, that is, the rotor, can also have concavities under the mixing ring, which can both be made to coincide with the openings in the mixing ring and disposed offset from them. These concavities can match the openings in the mixing ring in terms of their circumferential shape, or can differ from them in size and shape. Typically, the concavities have the shape of partial cutouts of a ball or ellipsoid, that is, they are hemispherical or half-ellipsoid concavities, and a fluid transition from the rotor surface and concavity is preferred over an abrupt, sharp-edged transition. Especially suitable embodiments of extruders or injection molding equipment containing a separate mixing ring that has openings are also described EP 340 873 B1 and German Patent DE 42 36 662 C2, which are hereby expressly incorporated by reference into the present disclosure.

The production of the film rear-injected plastic molded parts is preferably accomplished in a multistage process, by

- a) producing the film, in particular the composite laminated film, by means of adaptor or nozzle (co)extrusion of the cover, substrate layer and optionally intermediate layer, with the entire film composite either in a single- stage process or by laminating the individual layers to one other or by applying a radiation-curable cover layer to a single- or multi-layer film;
- b) optionally, thermoforming or deep-drawing of the composite laminated film in a molding tool; and
- c) rear injection of the composite laminated film with the fiber reinforced plastic material; the plastic material and fiber material is placed before the rear injection in an extruder or injection molding machine, which in the zone adjoining the compression zone has at least one distributive mixing element, and melted and mixed, and the chemical foaming agent is added directly to the plastic material jointly with the glass fibers, or after the addition of glass fiber in a downstream region to the plasticizer unit.

For the rear-pressing, the swell-flow method, the preforming method, or the strand deposition method can for instance be used. These methods are known to one skilled in the art and among other sources are described by Woite et al, in "Kunststoffe im Automobilbau: Rohstoffe, Bauteile, Systeme" [Plastics in Automobile Construction: Raw

Materials, Components, Systems], VDI-Verlag GmbH, Düsseldorf, 1994, pp. 280 to 313.

In the swell-flow method, the melt is introduced, with the tool open, through a hot channel system in the lower half of the tool, into the horizontal parting plane. Depending on the size of the component, it is also possible to have a plurality of injection points, which can optionally also be arranged in cascading form.

In the strand deposition method, a molten strand of composition from an extruder or an injection molding unit is applied to the lower half of the tool. The shaping process then ensues, by means of die stamping, using the film secured to the upper half of the tool.

In the preforming method, the molten molding composition placed in the tool is first placed in an appropriate pressing mold, and it is then processed using the actual upper tool to make the composite molded part.

In the rear-pressing process, the foaming agent is typically, similarly to the procedure described already for the rear injection process, mixed with the plastic material in the plasticizer unit and is then as a rule homogeneously distributed in the melt cake or melt strand introduced into the tool.

In the rear-pressing operation of the methods described, the tool temperatures are generally in the range from 20 to 80°C. The temperature of the plastic material in the tool depends on its melt temperature and is generally in the range from 200 to 280°C.

The pressures that occur in the rear-pressing are as a rule in the range from 100 to 300 bar.

In a further embodiment, the rear-pressing molding tool is subjected as a whole, at least for the period from the introduction of the melt to complete tool closure, to a pressure in a pressure chamber. This variant method is especially attractive in the swell-flow method, in which the melt is as a rule injected into the pressing tool that is opened with a gap width of only a few millimeters. A suitably high counterpressure at the level of the vapor pressure of the foaming agent at the processing temperature thus prevents the premature expulsion of the volatile components of the foaming agent.

The composite molded parts that can be obtained by the method of the invention are suitable for instance as interior or exterior vehicle body parts, as components for shipbuilding and aircraft construction, or as components for household or electrical appliances.

By the method of the invention, composite molded parts are obtained that have a less-

anisotropic mechanical and thermal property profile, or in other words particularly in terms of CTE value, fracture strength, elongation to break, impact toughness, and rigidity have very good values regardless of the testing direction. For example, CTE values in the range from 30 to 60×10^{-6} 1/K and elongation to break values in the range from 2 to 3%, and preferably 2.5 to 3%, and rigidities of 3000 to 6000 MPa, and preferably 3500 to 6000 MPa, can readily be attained, for instance with ABS polymer as the rear injection plastic material. Even under severe temperature stress, the composite molded parts of the invention have virtually no warping, if any. This is even true for large-area composite molded parts.

Even with partly crystalline plastic materials, such as polypropylene, polyethylene terephthalate, or polyamide, which typically cannot be foamed, or can be foamed only if purposeful modifications are made, for instance by branching or slight incipient cross-linking of the molecular chains to increase the melt viscosity (see also the foamed polypropylene known as Profax® made by Himont), composite molded parts that have all the aforementioned properties and that in particular lead to a weight reduction and at the same time are very rigid, have markedly less warping or no warping and have a Class-A surface can be obtained by the method of the invention.

In terms of the invention, a Class-A surface is understood hereinafter to mean a component surface on the side toward the foil that in terms of the frequency and size of flaws and in terms of gloss and color fastness and color uniformity is at least equivalent to conventional high-quality painted metal components, of the kind used in automobile construction.

Examples:

1. In a plastic material 1500 into an injection molding machine (Krauss Maffei; worm diameter, 115 mm), an ABS polymer (Terluran® weight-%-22, BASF AG) and, as a chemical foaming agent, 1 weight-%, referred to the total quantity of injection molding composition, of Hydrocerol® SK 35 (Boehringer Ingelheim KG) were metered in gravimetrically. Immediately after melting of the mixture, a glass fiber roving (R43SX6 made by OCF) was drawn in from the worm via a housing opening (15 weight-%, referred to the total weight of the injection molding composition). Downstream, the injection molding machine had shearing mixing elements, which mixed the glass fibers distributively with the melt. The melt temperature in the injection molding machine was in the range of 260°C, but no higher. The melts obtained were injected into a plate tool(1200 x 300 mm) with a lateral band gate behind a coextruded two-layer film, placed against one wall of the molding tool, of acrylic-coated Luran® S 778TE (cover layer, polymethyl methacrylate; substrate layer, ASA). The mechanical tests described below were performed on the composite molded parts obtained.

2. The procedure is as in Example 1, but first, cut glass with a starting length of 4 mm (Cratec® 152A14C made by OCF) and the plastic material, which was in granulate form, were mixed in a mixing system (made by Maguire) and then metered, jointly with the chemical foaming agent, into the inlet funnel of the injection molding machine.

3. The procedure is as in Example 2, but as the physical foaming agent, supercritical CO₂ (1 weight-%, referred to the injection molding composition) was injected via a piston pump into the metering zone of the plasticizer unit.

4. The procedure is as in Example 2, but as the plastic material, a glass-fiber-reinforced blend of PBT and ASA (Ultradur® S 4090 G6, BASF AG) was processed at a melt temperature of 270°C.

Examples 1 to 4 were repeated, but without using a foaming agent (Examples V1 to V4).

For all the composite molded parts obtained in accordance with Examples 1 through 4 and 1V to 4V, both tension and impact bending tests were performed. The rigidity, toughness and coefficient of thermal elongation were each determined both longitudinally and transversely to the flow direction of the melt in the composite molded part. The quotient of the aforementioned longitudinal and transverse characteristic values is a measure for the anisotropy of the composite molded parts. The lower this quotient is, the less is the anisotropy (the ideal value is 1).

The results are summarized in the table below:

Table:

Example	Rigidity ^{a)} Elongation ^{b)}	Longitudinal transverse/	Viscosity ^{c)}
	longitudinal/ transverse	longitudinal	longitudinal/ transverse
V1	1.27	1.80	1.12
1	1.13	1.45	1.06
V2	1.25	1.75	1.10
2	1.10	1.35	1.03
V3	1.25	1.75	1.10
3	1.08	1.30	1.05
V4	1.41	2.80	1.18
4	1.25	1.80	1.08

a) determined in accordance with ISO 527;

b) determined in accordance with DIN 53752;

c) determined in accordance with ISO 179/1fU.

Claims

1. A method for producing composite molded parts, wherein a) a single- or multi-layered film is inserted into a tool, b) which, if desired, is or will be deep-drawn or thermoformed, c) this film is rear-injected or rear-pressed during the injection molding or pressing process with a plastic material in melted form and containing a pore-forming foaming agent and fiber material, and d) the composite molded part is removed from the tool.
2. The method for producing composite molded parts in accordance with claim 1, characterized in that as the pressing method, the strand deposition, preforming, or swell-flow method is employed.
3. The method in accordance with claim 1 or 2, characterized in that a chemical foaming agent is used.
4. The method in accordance with claims 1 to 3, characterized in that induced thermally or by radiation, the foaming agent splits off volatile components.
5. The method in accordance with claims 1 to 4, characterized in that the splitting off of volatile components from the chemical foaming agents takes place completely or virtually completely not until after the introduction of the plastic material, containing foaming agent, into the molding tool.
6. The method in accordance with one of claims 1 to 5, characterized in that the single-layer film is formed of copolymers or of a mixture containing polyamides and polyethylene ionomers.
7. The method in accordance with one of claims 1 to 5, characterized in that the multi-layered film is composed, in this order, of at least one substrate layer (1), optionally at least one intermediate or decorative layer (2), and at least one transparent cover layer (3).
8. The method in accordance with claim 7, characterized in that the substrate layer (1) contains ASA polymers, ABS polymers, polycarbonates, polyesters, polyamides, polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers, or mixtures thereof; the intermediate layer (2) contains poly(meth)acrylates, high-impact poly(meth)acrylates, poly(meth)acrylamides, poly(meth)acrylonitrile, ASA polymers, ABS polymers, polycarbonates, polyesters, polyamides, polyether sulfones, polysulfones, polyvinyl chloride, or mixtures thereof; and the cover layer (3) contains poly(meth)acrylates, high-impact poly(meth)acrylates, fluoro(co)polymers, ABS polymers,

polycarbonates, polyethylene terephthalate, amorphous polyamide, SAN polymers, polyether sulfones, polysulfones, or mixtures thereof.

9. The method in accordance with claim 7, characterized in that the cover layer comprises a UV-cross-linkable resin.

10. The method in accordance with claims 1 to 9, characterized in that ASA polymers or ABS polymers, SAN polymers, poly(meth)acrylates, polyether sulfones, polybutylene terephthalate, thermoplastic polyurethanes, polycarbonates, polypropylene, polyethylene, or mixtures thereof, are used as the plastic material.

11. The method in accordance with claims 1 to 10, characterized in that glass fibers, carbon fibers or natural fibers are used as the fiber material.

12. The method in accordance with claims 2 to 11, characterized in that azodicarboxylic acid diamide, sulfohydrazides, semicarbazides, citric acid and its esters, peroxy, triazine, tetrazol, tetrazone or tetramine compounds, alkali or alkaline earth carbonates or bicarbonates, are used as chemical foaming agents, or ethanol, dimethylether, n- butane, n- or i-pentane, cyclopentane, fluorochlorinated hydrocarbons, carbon dioxide or nitrogen is used as physical foaming agents.

13. Composite molded parts obtained in accordance with one of claims 1 to 12.

14. Use of the composite molded parts in accordance with claim 13 as interior or exterior vehicle components, or as components for shipbuilding and aircraft construction or as components for household or electrical appliances.